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Urban water systems under climate stress: An isotopic perspective from Berlin, Germany

Lena-Marie Kuhlemann[1,2] | Doerthe Tetzlaff[1,2,3] | Chris Soulsby[3,1,4]

[1]Department of Ecohydrology, Leibniz Institute of Freshwater Ecology and Inland Fisheries (IGB), Berlin, Germany
[2]Department of Geography, Humboldt-University Berlin, Berlin, Germany
[3]Northern Rivers Institute, School of Geosciences, University of Aberdeen, Aberdeen, UK
[4]Chair of Water Resources Management and Modeling of Hydrosystems, Technical University Berlin, Berlin, Germany

Correspondence
Lena-Marie Kuhlemann, Leibniz Institute of Freshwater Ecology and Inland Fisheries (IGB), Berlin, Germany.
Email: kuhlemann@igb-berlin.de

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Abstract
Large urban areas are typically characterized by a mosaic of different land uses, with contrasting mixes of impermeable and permeable surfaces that alter "green" and "blue" water flux partitioning. Understanding water partitioning in such heterogeneous environments is challenging but crucial for maintaining a sustainable water management during future challenges of increasing urbanization and climate warming. Stable isotopes in water have outstanding potential to trace the partitioning of rainfall along different flow paths and identify surface water sources. While isotope studies are an established method in many experimental catchments, surprisingly few studies have been conducted in urban environments. Here, we performed synoptic sampling of isotopes in precipitation, surface water and groundwater across the complex city landscape of Berlin, Germany, for a large -scale overview of the spatio-temporal dynamics of urban water cycling. By integrating stable isotopes of water with other hydrogeochemical tracers we were able to identify contributions of groundwater, surface runoff during storm events and effluent discharge on streams with variable degrees of urbanization. We could also assess the influence of summer evaporation on the larger Spree and Havel rivers and local wetlands during the exceptionally warm and dry summers of 2018 and 2019. Our results demonstrate that using stable isotopes and hydrogeochemical data in urban areas has great potential to improve our understanding of water partitioning in complex, anthropogenically-affected landscapes. This can help to address research priorities needed to tackle future challenges in cities, including the deterioration of water quality and increasing water scarcity driven by climate warming, by improving the understanding of time-variant rainfall-runoff behaviour of urban streams, incorporating field data into ecohydrological models, and better quantifying urban evapotranspiration and groundwater recharge.

KEYWORDS
ecohydrology, hydrogeochemistry, isotopes, tracers, urban green spaces, urban hydrology

1 | INTRODUCTION

Today, more than half of the world's population and more than 70% of people in Europe live in urban areas (United Nations, 2019). Consequently, many metropolitan areas face considerable challenges in covering their increasing water demand, which often leads to the overexploitation of local water resources and the need to import water from remote areas (e.g. Good et al., 2014; Jago-On et al., 2009). By 2050, it is expected that around 27% of the cities worldwide could be facing a water demand that exceeds their surface water availability while another 19% could face competing interests between urban and agricultural water demands (Floerke, Schneider, & McDonald, 2018). To secure a sustainable water supply in the future, as well as to mitigate flood hazards from urban runoff (e.g. Konrad, 2013) and to maintain dry weather flows to sustain aquatic ecosystems and safely dilute waste water effluents (e.g. Englert, Zubrod, Schulz, & Bundschuh, 2013; Gücker, Brauns, & Pusch, 2006), integrated management of urban water resources is crucial. This requires process-based understanding of water sources in urban water bodies and insight into the interactions between engineered hydrosystems in built-up areas and more natural hydrosystems in urban green spaces (Gessner et al., 2014; McGrane, 2016). It is well-known that urbanization has a significant impact on catchment hydrology. Urbanization tends to increase direct runoff from impervious areas and artificial storm drains during rainfall events; reduce infiltration, groundwater recharge and baseflow; and increase the influence of waste water effluents (Endreny, 2005; Fletcher, Andrieu, & Hamel, 2013). However, other studies show that imperviousness and reduced evaporation can increase localized infiltration and, along with gains from underground pipe leakage, increase groundwater recharge (Lerner, 2002; Schirmer, Leschik, & Musolff, 2013). Although specific impacts of urbanization on streams can differ between regions and climates (Brown et al., 2009; Hale, Scoggins, Smucker, & Such, 2016), the general patterns of flashier hydrographs, deterioration of water quality, increased nutrient loads, and degraded channel morphology – which together lead to a loss of biotic richness – has been termed the "urban stream syndrome" and observed in cities around the world (Booth, Roy, Smith, & Capps, 2016; Walsh et al., 2005).

The heterogeneity of urban areas and their hinterlands, together with a long history of engineering and environmental management, often leads to evolving, complex hydrological systems that are fragmented, sparsely monitored and poorly understood. Useful, integrating tools to investigate water sources and fluxes in the hydrological cycle are environmental tracers. Stable isotopes in water, for example, are affected by meteorological inputs and provide characteristic "fingerprints" of water's origin and flow paths (Clark & Fritz, 1997). Unlike most chemical tracers, isotopes behave conservatively and can provide integrated insights into the relative importance of different water sources contributing to stream flow; the sources, timing and location of groundwater recharge; hydraulic connections between groundwater and surface water; as well as evidence of evaporation and transpiration (Kendall & McDonnell, 1998). Their potential to elucidate spatio-temporal patterns has recently been highlighted as a means for understanding and managing anthropogenic impacts on the urban hydrological cycle (Ehleringer, Barnette, Jameel, Tipple, & Bowen, 2016).

Previous isotope studies are surprisingly scarce in urban areas, but have provided insights into stormwater-stream dynamics (Jefferson, Bell, Clinton, & McMillan, 2015) and a basis for estimating transit time distributions (Parajulee, Wania, & Mitchell, 2019; Soulsby, Birkel, Geris, & Tetzlaff, 2015; Soulsby, Birkel, & Tetzlaff, 2014). Combined with hydrochemical tracers and modelling, they have been used to quantify the role of groundwater in urban water systems. For example, Houhou et al. (2010) detected (ground-) water seepage into an urban sewer system, showing infiltration "hot spots" in relation to wastewater flow rates. Through spatio-temporal surveys in the urbanized Jordan River Basin in Utah, Follstad Shah et al. (2019) demonstrated the important role of groundwater as a contributor to urban surface waters, despite the influence of engineered water inputs like wastewater effluents. Further, it was revealed that land use and infiltration rate can impact shallow aquifer systems affected by the urban heat island (UHI) effect (Salem, Taniguchi, & Sakura, 2004). Groundwater as an active component of the urban water cycle with rapid recharge and significant discharge into urban streams has been identified by Meriano, Howard, and Eyles (2011) in the 75% urbanized Frenchman's Bay study area in Canada. In central Ethiopia, spatial isotopic variations have been successfully utilized to distinguish groundwater systems with different lithologies, residence times and anthropogenic influences (Demlie, Wohnlich, & Ayenew, 2008). Spatially distributed isotopic landscape maps (isoscapes) have shown how isotopic variations can be used in urban hydrology to investigate dominant mechanisms of water transport and effects of evaporation/condensation (Bowen, 2010; Bowen et al., 2009). Such maps have helped constrain drinking water sources in complex urban distribution networks, depending on seasonality, population density or water system structure, both locally (e.g. Jameel et al., 2016; Tipple et al., 2017) and at large scales (e.g. Bowen, Ehleringer, Chesson, Stange, & Cerling, 2007; Landwehr, Coplen, & Stewart, 2014).

Whilst such studies demonstrate the potential of isotopes in urban hydrology, there remain considerable research gaps. In particular, conducting field studies across the landscape of larger cities remains challenging. This is because constraining water fluxes in complex urban areas, with heterogeneity in land cover distribution, subsurface flow paths, recharge conditions and contaminant patterns (Fletcher et al., 2013; Schirmer et al., 2013) requires monitoring extensive spatio-temporal scales, which is hard to maintain by local authorities or researchers. Furthermore, river flow generated upstream of the built-up area often interacts with local streams and waste water discharged from domestic and industrial users, but also with local groundwater resources and sewer systems draining cities. In older conurbations, the relative contributions of these different sources are often not well-understood qualitatively and the identification of water sources is needed to understand how anthropogenic impacts alter the urban hydrological cycle as water moves through the urban system (Ehleringer et al., 2016). As the need for more sustainable approaches to managing urban waters grows, such an understanding of how natural and engineered hydrological systems combine in cities is crucial to the evidence-base for rational decision making (Follstad Shah et al., 2019; Gessner et al., 2014; McGrane, 2016).

The overarching goal of this study is to use isotope-based surveys in the city of Berlin to identify dominant seasonal water sources and flow paths. Berlin, the 891 km^2 large German capital has a population of 3.64 million that is growing by around 1% per year (Amt für Statistik Berlin-Brandenburg, 2019). It provides an exceptional setting for this study as it is characterized by (a) a water management system that is highly dependent on local sources of surface- and ground water (Limberg et al., 2007; Limberg & Thierbach, 1997; Möller & Burgschweiger, 2008), (b) low precipitation and evaporation as the dominant flux of water, with an average annual "blue water flux" of groundwater recharge being <155 mm (or <30% of precipitation; Limberg et al., 2007), (c) a highly variable land use, with extensive impermeable cover affecting over 60% of some areas of the city centre (Senate Department for Urban Development and Housing [SenStadtWoh], 2017) and large areas of urban green spaces (including forests), and (d) various anthropogenic impacts on its water cycle, including a range of abstractions, waste water treatment plants and industrial discharges. The specific objectives of this study are: (a) to characterize Berlin's temporal isotope dynamics in precipitation and streamwater over the course of 1 year, (b) to identify the spatio-temporal patterns of isotopes in Berlin's surface and subsurface waters during different seasons and wetness conditions and (c) to integrate stable isotope and other hydrogeochemistry data to assess how key urban processes like evaporation, storm water runoff and effluent discharge interact in a time-variant way to influence stream flow.

2 | STUDY SITE

Berlin is located in the Northern European glaciation plain and is characterized by a flat topography (Figure 1a,b) resulting from the Pleistocene glaciation. Around 95% of the surface geology comprises Quaternary deposits (Stackebrandt & Manhenke, 2010).

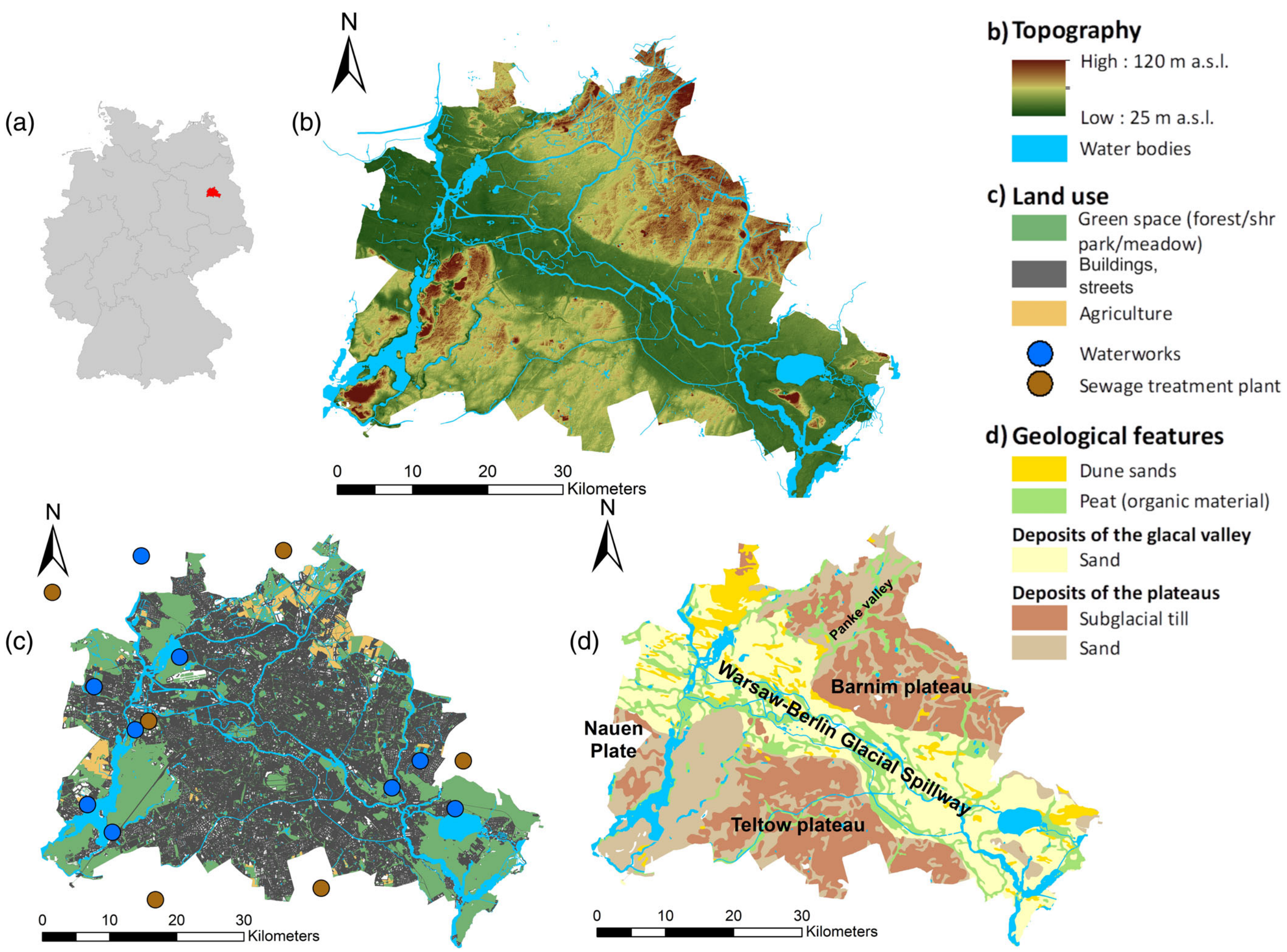

FIGURE 1 (a) Location of Berlin within Germany, (b) Berlin's topographic structure and surface water system; (c) land use types including the waterworks and sewage treatment plants in and around the city's boundaries (BWB, 2019a); and (d) geology. Data source basemaps: BGR (2007); GeoBasis-DE/BKG (2013, 2019)

These surficial deposits are predominantly sands and gravels in the Berlin-Warsaw-Glacial Spillway orientated NW to SE, with the secondary Panke valley in the North (Limberg et al., 2007; Senate Department for Urban Planning and the Environment [SenStadtUm], 2013a; Figure 1d). The fringing plateaus of Barnim (North) and Teltow (South) and the Nauen Plate are covered by subglacial till (Limberg et al., 2007; SenStadtUm, 2013a; Figure 1d).

The city is underlain by a several hundred meter thick lower saline aquifer and an upper freshwater aquifer of Tertiary to Holocene age with average thickness of 150 m (Limberg & Thierbach, 1997). The freshwater aquifer is sub-divided into layers of unconsolidated sands and gravels, separated by mud, clay, silt and till layers, with occasional hydraulic connection (Limberg et al., 2007; Limberg & Thierbach, 1997, 2002). Horizontal groundwater flow is directed from the Barnim and Teltow plateaus and the Nauen Plate towards the rivers Spree and Havel with velocities of 10–500 m per year (Limberg et al., 2007). Groundwater heads are high and usually only up to 4 m below the surface (b.s.) in the glacial valley, while they are >10 m b.s. on the plateaus (Limberg et al., 2007).

Large areas of Berlin are covered by urban green spaces, including forest (18.1%), public green space (12.2%) and agricultural areas (4.2%), particularly towards the outer boundaries (Senate Department for the Environment, Transport and Climate Protection [SenUVK], 2018; Figure 1c). Almost 60% of the city is covered by buildings and roads (SenUVK, 2018; Figure 1c), of which around 34% are sealed, especially in the centre (SenStadtWoh, 2017).

Climatically, Berlin lies in a dry part of Germany. Mean annual rainfall (1981–2010) of Berlin's weather stations run by the German weather service (Deutscher Wetterdienst [DWD], see Figure 2) ranges from 525 to 593 mm (DWD, 2019b). Mean annual air temperature ranges from 9.3 to 10.0°C (1981–2010; DWD, 2019b). On average, 56% of rainfall is evapotranspired, 12% enter surface waters through surface runoff and artificial drainage networks, 5% enter surface waters via diffuse subsurface runoff and 27% become groundwater recharge (Limberg et al., 2007). Despite low recharge, there are numerous lakes and wetlands due to Berlin's complex glacial drift deposits (Gerstengarbe et al., 2003).

Berlin's major surface water bodies are (a) the Spree, which enters as the Müggelspree in the East, joining with the Dahme in the Southeast, before flowing westwards through the city, and (b) the south-flowing Havel, which enters from the Northwest before joining the

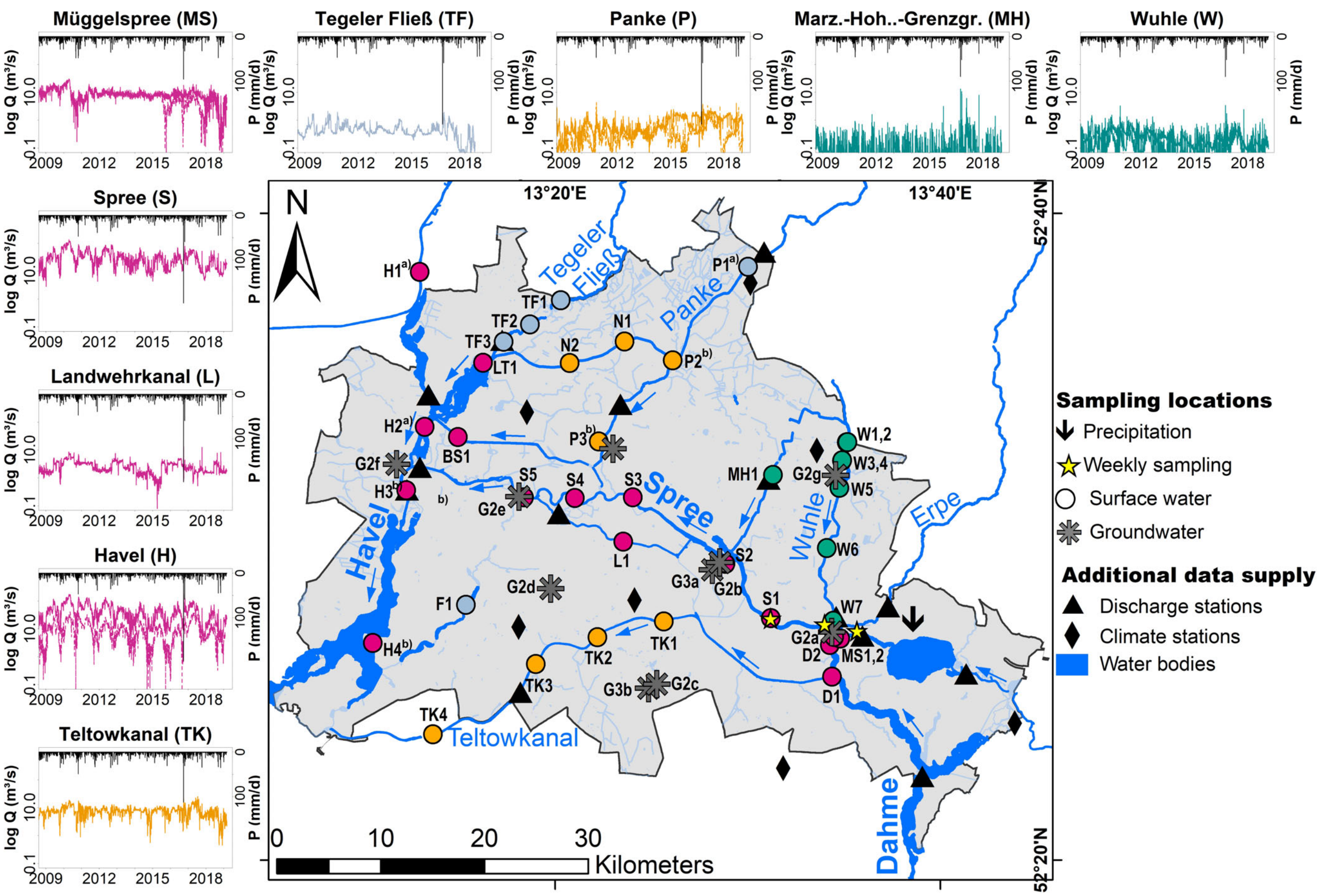

FIGURE 2 Long-term discharge (SenUVK, 2019) and climate data (DWD, 2019a) in the study area with sampling locations of the seasonal field campaigns: Major surface waters (maroon), effluent-impacted streams (orange), local wetland-impacted streams (light blue), local urban streams (cyan) and groundwater (grey asterisk). Locations of weekly stream water and daily precipitation sampling are marked in the eastern study area. Data source basemap: GeoBasis-DE/BKG (2013)

Spree (Figure 2). Both rivers have low slopes and flow through wetlands (e.g. Spreewald) and lakes (e.g. Müggelsee; Jahn, 1998; Senate Department for Urban Planning [SenStadt], 2004). The Spree drains a catchment of ~10,000 km^2, >90% of this upstream of the city, including the Dahme catchment of around 2,200 km^2, and is subject to anthropogenic abstractions, for example, for irrigation, industry and lignite mining (Jahn, 1998; Limberg et al., 2007; SenStadt, 2004). Within Berlin, ~13% of the catchment is sealed and connected to storm drains (SenStadtWoh, 2018; Table 1). Some artificial navigation channels with intermediate discharge (Figure 2, Table 3) withdraw water from the Spree and Dahme, including the Landwehrkanal, Teltowkanal and the Berlin-Spandauer-Schiffahrtskanal. The Havel drains a catchment of ~3,500 km^2 at the Spree confluence (Jahn, 1998; SenStadt, 2004). Discharge rates of both rivers can be low, especially during summer (Jahn, 1998; Limberg et al., 2007). Several local tributaries enter the Spree from the north, including the Panke, Wuhle and Erpe (Figure 2). These streams are characterized by significantly lower discharge rates (Figure 2, Table 3), with catchments of varying land covers and degrees of urbanization. Highly urbanized streams include the Wuhle, for which ~14% of the catchment in Berlin is sealed and connected to stormwater drains, and the Marzahn-Hohenschönhausener-Grenzgraben with an enterily urban and 30% sealed catchment (Table 1). Others are less urbanized and can be impacted by fen soils, for example, the catchments of the Tegeler Fließ, Erpe, Fenngraben and the northern parts of the Panke (SenStadtUm, 2015).

To provide Berlin's water supply, nine waterworks (Figure 1c) abstract water mainly from groundwater pumping of the freshwater aquifer (Limberg & Thierbach, 1997). Around 60% of this is generated by well galleries near the riverbank that draw water from surface water bodies through bank filtration (Limberg et al., 2007; Möller & Burgschweiger, 2008). As a result, Berlin's drinking water supply is highly dependent on the quantity and quality of streams like the Havel, Spree and Dahme (Möller & Burgschweiger, 2008). At the same time, urban storm water drainage, combined sewer overflows (CSO) and the city's sewage treatment plants (Figure 1c) discharge water into these streams (Möller & Burgschweiger, 2008; Riechel, 2009; Weyrauch et al., 2010). Major recipients of stormwater drainage are the Teltowkanal (long-term mean 13 Mio. m^3 per year), the Wuhle and the downstream part of the Panke (long-term mean inputs of 3 Mio. m^3 respectively; SenStadtWoh, 2018). CSOs from the combined sewer system that accounts for around 20% of the city's subsurface drainage area, especially in the centre, contribute around 7 million m^3 of water per year to the Spree (Weyrauch et al., 2010) and can account for up to 10% to its total volume during low flow periods in the summer (Riechel, 2009). Streams strongly impacted by treated sewage water released by Berlin's treatment plants (Figure 1c) include the Nordgraben in the Northwest and the Teltowkanal in the

TABLE 1 Streams assigned to the sampling groups with their respective Sample IDs, number of seasonal sampling locations; and total catchment size and catchment size within Berlin with % of the Berlin catchment sealed and connected to the drainage system, based on data from SenStadt, 2004, and SenStadtWoh, 2018

Stream		ID	Sampling locations	Catchment area (km^2)	Catchment in Berlin (km^2) (% sealed)
Major surface waters					
Dahme		D	2	See below (spree)	
(Müggel-) spree		(M)S	(2+) 5	10,105	174 (13)
Landwehrkanal		L	1	26	26 (15)
Berlin-Spandauer-Schiffahrtskanal		BS	1	n.a.	n.a.
Lake Tegel		LT	1	150	n.a.
Havel	(a)	H	2	3,500	n.a.
	(b)		2		n.a.
Local wetland-impacted streams					
Tegeler Fließ		TF	3	172	80
Fenngraben		F	1	n.a.	n.a.
Panke	(a)	P	1	See below	
Local urban streams					
Wuhle		W	7	101	57 (14)
Marzahn-Hohensch.-Grenzgraben		MH	1	23	23 (30)
Effluent-impacted streams					
Panke	(b)	P	2	198	47 (16)
Nordgraben		N	2	34	32 (13)
Teltowkanal		TK	4	243	166 (16)
Erpe		–	1 (weekly)	222	14 (n.a.)

Note: Locations marked (a) at entry into the city area and (b) further downstream.

TABLE 2 Mean air temperature and precipitation sums in the 3 months preceding the seasonal sampling campaigns calculated from daily data of all seven DWD climate stations in and around Berlin (DWD, 2019a; see Figure 2)

Mean daily air temperature (°C)				Sum of mean daily precipitation amounts (mm)			
Jul-Oct 18	Nov-Jan 19	Feb-May 19	May-Jul 19	Jul-Oct 18	Nov-Jan 19	Feb-May 19	May-Jul 19
18.5	4.8	8.3	18.3	37.9	115.7	90.2	170.8

TABLE 3 Long-term (10 years) mean, percentiles, SD and coefficient of variation (CV) of daily discharge rates and mean discharge rates 3 months before the respective sampling campaigns calculated with data (SenUVK, 2019) from the discharge stations shown in Figure 2

		Long-term discharge (m^3/s)					Mean daily discharge 3 months before sampling (m^3/s)			
Stream		Mean	Fifth percentile	95th percentile	SD	CV	Jul-Oct 18	Nov-Jan 19	Feb-May 19	May-Jul 19
Major surface waters										
Dahme		15.8	2.3	43.7	12.8	0.8	4.1	7.7	9.5	5.1
Müggelspree	(a)	3.6	0.5	6.8	2.0	0.6	1.2	3.9	4.8	1.5
	(b)	8.8	2.7	16.6	4.3	0.5	5.1	6.8	6.9	2.0
Spree		32.1	8.1	76.2	21.8	0.7	8.6	20.6	24.7	11.3
Landwehrkanal		2.6	1.0	4.9	1.3	0.5	1.7	1.6	2.7	2.6
Havel	(a)	9.9	1.5	26.1	7.6	0.8	4.3	7.8	8.5	4.0
	b)	44.2	7.7	105.0	31.4	0.7	8.6	24.9	31.5	11.6
Local wetland-impacted streams										
Tegeler Fließ		0.5	0.1	1.0	0.3	0.6	0.1	0.3	0.2	0.1
Panke	(a)	0.4	0.1	1.0	0.3	0.9	0.1	0.2	0.3	0.5
Local urban streams										
Wuhle		0.3	0.1	0.7	0.2	0.7	0.1	0.2	0.2	0.2
Marz.-Hohensch.-Grenzgr.		0.1	0.0	0.4	0.4	4.2	0.01	0.1	0.1	0.1
Effluent-impacted streams										
Panke	(b)	0.8	0.2	1.8	0.5	0.6	1.1	1.4	1.0	0.9
Nordgraben		1.3	0.2	2.5	0.8	0.6	0.2	0.3	1.1	1.0
Teltowkanal		7.8	2.7	13.5	3.1	0.4	5.0	6.4	6.6	4.1
Erpe		1.0	0.4	2.0	0.5	0.6	0.4	0.8	0.9	0.5

Note: Locations marked (a) at entry into the city area and (b) further downstream.

South (Figure 2). Amounts of treated wastewater were quantified to be up to 5% for the Spree, 18% for the Havel (after the Spree confluence), up to 50% in the Teltowkanal and around 89% in the Nordgraben under normal flows; increasing to 100% in the Havel, Teltowkanal, Nordgraben and Erpe and up to 30% in the Spree during low flows (Drewes, Karakurt, Schmid, Bachmaier, & Hübner, 2018). Similar observations were made by Massmann, Knappe, Richter, and Pekdeger (2004).

3 | METHODOLOGY AND DATA

Daily air temperature and precipitation data was available from seven DWD weather stations in Berlin (DWD, 2019a). Mean daily stream discharge data was provided by the Senate Department for the Environment, Transport and Climate Protection (SenUVK, 2019) and daily discharge data of Berlin's treatment plants by the Berlin waterworks (Berliner Wasserbetriebe [BWB], 2019b).

Data collection focused on 1 year (October 2018–October 2019). For temporal isotope dynamics in precipitation and streamwater, high-resolution sampling was undertaken in eastern Berlin (Figure 2). In Berlin-Friedrichshagen, daily precipitation isotope samples were collected using a HDPE deposition sampler (100 cm^2 opening; Umwelt-Geräte Technik GmbH). Overall, 35 daily and 35 bulk (interval > 24 hours, e.g. weekends) samples where precipitation was >1 mm (to limit evaporation effects) were collected. Stream samples were taken weekly using a polyethylene collector lowered from bridges at three sites: the Spree downstream of the Dahme confluence, the urbanized Wuhle near its catchment outlet and the effluent-impacted Erpe (Figure 2).

To characterize the spatial isotope patterns of Berlin's surface and subsurface waters, four synoptic field campaigns were undertaken at pre-selected locations in October 2018 (31 sites) and in January, May and July 2019 (37 sites). Surface waters were categorized into four groups: major surface waters with high/intermediate discharge, local wetland-impacted- and local urban streams with low discharge, and effluent-impacted streams (Figure 2, Table 1). All sites were sampled over 1 day in each survey and analysed for stable isotopes, major- and trace elements. From the second survey, hydrogeochemical parameters were measured on-site using a WTW Multi 3,630 IDS Set for pH (SenTix940, precision ±0.004), dissolved oxygen (DO; FDO925, precision ±0.5% DO; ± 0.2°C temperature) and electrical conductivity (EC; TetraCon925, precision ±0.5%). During the first sampling, pH and EC were measured in the lab.

Additionally, groundwater wells managed by Berlin Senate were sampled in the days following the surface water campaigns. The wells were spatially distributed and close to the surface water sampling points. Sampling included seven wells in different units of the freshwater aquifer system, primarily along the course of the glacial valley, from the second sampling on; with additional wells on the Barnim and Teltow plateaus (G2c,g; G3b) from the third sampling on (Figure 2). Groundwater levels were measured using an electric contact gauge. Depending on initial water level (range 2.4–4.8 m b.s. in the glacial valley and 5.4–12.3 m b.s. on the plateaus), water was pumped with a Comet Geo-Duplos Plus submersible pump (for shallow water tables) or a Grundfos MP1 submersible pump (for water tables >7 m b.s.). The pumped water was channelled through a polyethylene collector for 15–30 minutes while monitoring hydrochemical parameters with the WTW Multi 3,630 until the composition stabilized before the samples were taken. All samples were filtered on-site (0.2 μm), transported in a thermally isolated box and stored in the refrigerator until analysis. Overall, 228 surface and 25 groundwater samples were analysed.

For isotope analysis, samples were decanted into 1.5 ml glass vials (LLG Labware) and analysed by Cavity Ring-Down Spectroscopy with a L2130-i Isotopic Water Analyser (Picarro, Inc., Santa Clara, CA) using four standards for a linear correction function and standards of the International Atomic Energy Agency (IAEA) for calibration. After quality-checking and averaging multiple analyses for each sample, the results were expressed in δ-notation with Vienna Standard Mean Ocean Water (VSMOW). Analytical precision was 0.05 ‰ standard deviation (SD) for $\delta^{18}O$ and 0.14 ‰ SD for δD.

Samples for dissolved Cl^- and SO_4^{2-} were taken in 2 ml Eppendorf tubes and analysed by ion chromatography (Metrohm CompactIC, conductivity detection after chemical suppression). For analysis of Al, B, Ca, Fe, K, Mg, Mn, Na, P, S and Si, samples were taken in in 15 ml Cellstar tubes, acidified with 150 μl of 2 M HCl and analysed by inductively-coupled-optical emission spectroscopy (ICP-OES, Thermo Scientific iCAP 6300). Dissolved inorganic carbon (DIC) samples were analysed with a Shimadzu TOC-L Total Organic Carbon Analyser. Analytical precision was <3%.

Data processing and plotting used R Studio Version 1.2.5019. For the isotope samples, deuterium (d-) excess was calculated as $d = \delta D - 8 \cdot \delta^{18}O$ (Dansgaard, 1964). A local meteoric water line (LMWL) was calculated from daily samples by amount-weighted least square regression (Hughes & Crawford, 2012). Evaporation lines (EL) for all surface water samples were calculated by least-square regression. Major ion concentrations were converted to equivalents (meq/L) and samples with an ionic balance error > 10% were excluded from further processing. Long-term mean stream discharge, its percentiles, SD and coefficient of variation (CV) for the sampled streams as well as mean discharge, air temperature and sums of precipitation 3 months prior to sampling were calculated. The same was done for the precipitation isotopes. For statistical comparison of seasonal isotope data, minimum and maximum values, arithmetic means, medians and the fifth and 95th percentiles were calculated for the different stream groups. To combine isotope and hydrogeochemical data, a principal component analysis (PCA) was performed. Maps were created using Esri ArcGIS 10.7.

4 | RESULTS

4.1 | Temporal dynamics in precipitation and streamwater isotopes

The start of sampling in October 2018 followed an unusually warm, dry summer which was part of a major European drought. As a result of low precipitation with <40 mm in the 3 months preceding the first survey (Table 2), discharge the Spree was extremely low with a daily mean < 10 m^3/s (Figure 3, Table 3).

Discharge in all surface waters remained low until December, following relatively little rain. Some smaller rainfall events totalling >100 mm by the second survey in January 2019 (Table 2) increased most discharge rates (Figure 3, Table 3). More rainfall from February–May 2019 resulted in the highest discharges of the year in the time preceding the third survey. However, these values remained lower than the long-term means for the Spree and most of the major surface waters (Table 3). From May–October 2019, another dry summer occurred. In contrast to the previous year, 2019 was characterized by several heavy convective summer rainfall events with up to 55 mm on the 11th of June (DWD, 2019a), contributing to a total amount of ∼171 mm between May and July (Table 2). This led to a peak daily discharges of 43 m^3/s (12th of June) in the Spree (SenUVK, 2019; Figure 3). However, as most rain fell in short events, discharge in most major streams in July was only slightly higher than October 2018 (Table 3). Overall, seasonal changes in discharge were low in smaller local and effluent-impacted streams (Table 3). In the three streams sampled weekly, the more urbanized Wuhle showed a more marked response to precipitation events than the more stable Erpe (Figure 3).

High frequency sampling showed that daily precipitation isotope ratios in Berlin-Friedrichshagen ranged from −15.6 to −1.6 ‰ for $\delta^{18}O$ and from −118.1 to −8.3 ‰ for δD. There was a seasonal trend with more depleted signatures in winter and more enriched signatures in autumn 2018 and summer 2019 (Table 4). However, daily variability was marked in both winter and summer.

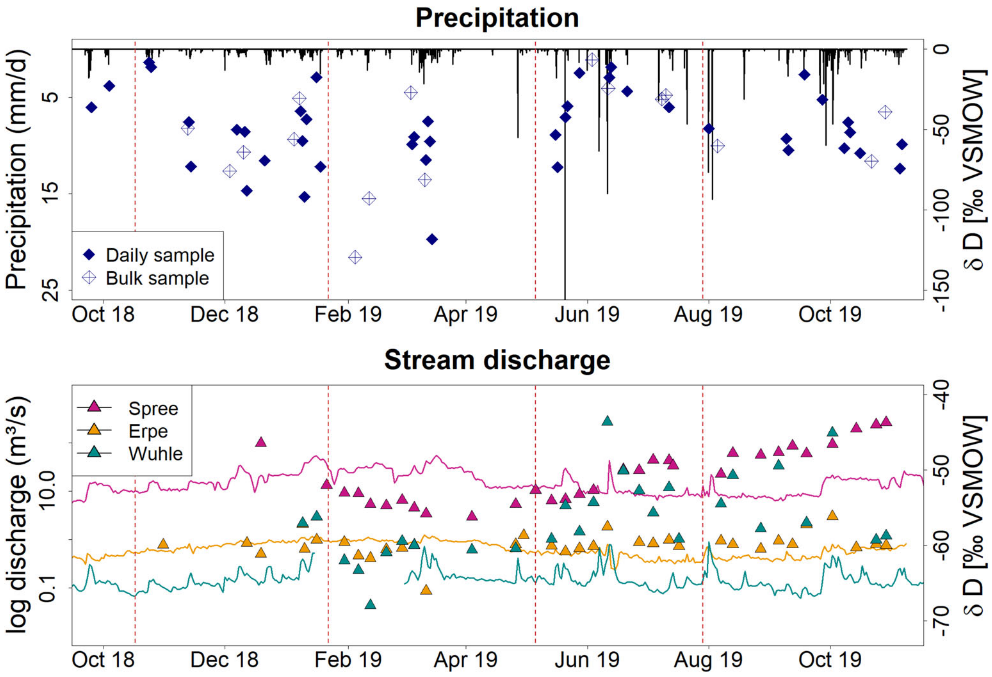

FIGURE 3 Precipitation events with stable isotopic composition of precipitation in Berlin-Friedrichshagen (top) and stream discharge (daily means, SenUVK, 2019) with stream water isotopic composition of the Spree, Wuhle and the effluent-impacted Erpe sampled on a weekly basis (bottom)

The LMWL (Figure 4, Figure 5) was close to the Global Meteoric Water Line (GMWL; Craig, 1961):

$$\delta D = 7.97 \pm 0.19\, \delta^{18}O + 11.37 \pm 1.59 \left(R^2 = 0.979\right).$$

As expected, stream water isotopes were much more damped than precipitation isotopes. Between the three streams sampled weekly, signatures were more enriched in the Spree with mean values of −6.7 (±0.8) ‰ for $\delta^{18}O$ and −50.6 (±3.7) ‰ for δD. Isotopes in the Spree followed a damped seasonal trend with winter depletion until April 2019, enriching thereafter (Figure 3). The Spree's EL shows a high explanatory power (R^2 = 0.99) and plots below the GMWL and LMWL (Figure 4). In the Wuhle, isotopes were more depleted with means of −7.9 (±0.98) ‰ for $\delta^{18}O$ and −57.2 (±6.7) ‰ for δD. However, isotopes were more dynamic and varied considerably over short time periods (Figure 3). The resulting EL of the Wuhle is less pronounced (Figure 4). Consistent with the stable discharge, the effluent-impacted Erpe was characterized by a more constant isotopic composition. Similar to the Wuhle, mean values were depleted with −8.2 ‰ for $\delta^{18}O$ and −59.9 ‰ for δD. However, variations were lower (SD 0.3 and 1.6 ‰ for $\delta^{18}O$ and δD, respectively), especially in 2019, where changes were only detected in response to heavier rainfall (Figure 3).

4.2 | Seasonal synoptic isotope sampling: Spatial patterns

Variations in climate, discharge and precipitation isotopes were also reflected in seasonal sampling campaigns. Isotopic signatures of major surface water bodies were most enriched during the warm, dry periods of October 2018 and July 2019 with mean values of up to −5.2 ‰ for $\delta^{18}O$, −44.3 ‰ for δD and negative mean d-excess down to −2.4 ‰ (Table 4, Figure 5). In contrast, the most depleted isotopic compositions were measured in May 2019 with mean $\delta^{18}O$ of −6.7 ‰, mean δD of −50.8 ‰ (Table 4). Effluent-impacted streams were most enriched in October 2018 and most depleted in January. Seasonal variations were low with mean $\delta^{18}O$ ranging from −7.3 to −6.9 ‰, mean δD between −54.4 and −52.5 ‰ and mean d-excess between 2.4 and 4.4 ‰ (Table 4). The wetland-impacted local streams showed the most enriched isotopic samples in July 2019 with mean values of −5.2 ‰ for $\delta^{18}O$, −43.1 ‰ for δD and −1.8 ‰ for d-excess (Table 4). The values in October 2018 were more depleted. In contrast to major surface waters, the most depleted values in these streams were measured in January 2019 with a mean $\delta^{18}O$ of −7.1 ‰ and mean δD of −54.4 ‰ (Table 4) when SDs were also high. The local urban streams were more depleted and had lower seasonal variations. Mean values ranged from −8.3 ‰ for $\delta^{18}O$ and −58.2 ‰ for δD in January to −7.4 ‰ for $\delta^{18}O$ and −53.0 ‰ in May 2019. D-excess was positive during all seasons with mean values between 4.5 ‰ in July and 8.1 ‰ in January. The isotopic composition of groundwater was similar to local urban streams, but even more depleted with mean values between −8.1 and −8.5 ‰ for $\delta^{18}O$, −61.0 and −58.9 ‰ for δD and 6.3–8.3 ‰ for d-excess (Table 4). Clear spatial or temporal trends were not evident, although samples from the Barnim and Teltow plateaus were slightly more depleted those from the glacial valley.

Plotting data from all seasonal sampling campaigns in the dual isotope space (Figure 5) revealed distinct differences (persisting beyond seasonal variations) between the more enriched major and local wetland-impacted streams, and the more depleted local urban streams and groundwater. Strongly effluent-impacted streams were intermediate. Surface water samples have an EL of δD = 4.85 ± 0.07 $\delta^{18}O$ −

TABLE 4 Measured isotopic composition of precipitation in the respective 3 months preceding the seasonal sampling campaigns and measured isotopic composition in the different stream types and groundwater during the four seasonal sampling campaigns

	$\delta^{18}O$ (‰ VSMOW)				δD (‰ VSMOW)				d-excess (‰ VSMOW)			
	Oct 18	Jan 19	May 19	Jul 19	Oct 18	Jan 19	May 19	Jul 19	Oct 18	Jan 19	May 19	Jul 19
Precipitation Berlin-Friedrichshagen												
n	4	14	6	9	4	14	6	9	4	14	6	9
Min.	−6.4	−12.7	−15.6	−10.7	−36.3	−91.9	−118.1	−73.5	7.7	4.3	6.4	−2.2
Fifth percentile	−6.3	−12.5	−14.3	−9.8	−36.1	−89.5	−105.9	−65.4	7.9	7.6	6.8	−1.4
Mean	−5.1	−7.8	−9.7	−5.3	−29.5	−51.4	−67.3	−34.6	11.6	11.4	10.4	7.6
Median	−5.0	−7.6	−8.7	−5.0	−29.4	−50.8	−58.3	−35.5	11.8	11.3	10.2	7.6
95th percentile	−4.2	−2.8	−7.1	−1.9	−23.1	−10.2	−47.4	−12.8	15.1	14.3	13.8	14.1
Max.	−4.1	−2.7	−6.8	−1.6	−22.9	−8.3	−45.0	−11.4	15.2	14.3	13.8	14.6
SD	1.0	3.3	3.1	3.0	7.0	26.5	26.1	20.0	3.9	2.7	3.0	6.1
Major surface waters (Dahme, (Müggel-) Spree, Havel, Lake Tegel, Landwehrkanal, Berlin-Spandauer-Schiffahrtskanal)												
n	14	16	16	16	14	16	16	16	14	16	16	16
Min.	−5.8	−7.0	−7.2	−7.4	−47.0	−52.5	−54.2	−55.0	−4.1	−0.6	0.5	−3.0
Fifth percentile	−5.8	−7.0	−7.1	−6.7	−46.9	−52.4	−53.4	−52.1	−3.5	0.2	1.2	−2.9
Mean	−5.2	−6.4	−6.7	−5.9	−44.3	−49.3	−50.8	−47.3	−2.4	2.0	3.0	−0.5
Median	−5.3	−6.6	−6.9	−6.0	−45.0	−50.7	−52.0	−48.8	−2.4	2.2	3.3	−0.3
95th percentile	−4.6	−5.4	−5.8	−4.7	−39.5	−43.4	−44.7	−40.6	−0.6	3.4	4.4	3.9
Max.	−4.5	−5.5	−5.8	−4.7	−39.3	−43.7	−44.9	−40.8	−0.5	3.4	4.2	1.9
SD	0.4	0.5	0.5	0.7	2.4	3.2	3.0	4.2	1.0	1.1	1.1	1.8
Local wetland-impacted streams (Tegeler Fließ, Fenngraben, Panke[a)])												
n	4	5	3	5	4	5	3	5	3	5	3	5
Min.	−8.7	−8.6	−6.8	−7.8	−60.4	−59.8	−50.2	−53.8	−3.6	−2.4	2.9	−5.9
Fifth percentile	−8.4	−8.4	−6.8	−7.4	−59.3	−58.9	−50.1	−52.4	−3.3	−1.0	2.9	−5.8
Mean	−6.6	−7.1	−6.6	−5.2	−51.0	−52.4	−49.3	−43.1	1.9	4.6	3.5	−1.8
Median	−6.3	−7.2	−6.5	−4.4	−49.6	−52.3	−49.1	−40.8	1.1	5.1	3.3	−5.3
95th percentile	−5.2	−5.4	−6.5	−3.7	−44.7	−44.5	−48.7	−35.5	8.1	8.5	4.2	6.5
Max.	−5.1	−5.0	−6.4	−3.6	−44.4	−42.8	−48.6	−34.5	8.9	9.0	4.3	8.3
SD	1.6	1.3	0.2	1.7	7.2	6.3	0.8	7.5	5.6	4.3	0.7	6.1
Local urban streams (Wuhle, Marzahn-Hohenschönhausener-Grenzgraben)												
n	7	7	8	4	7	7	8	4	7	7	8	4
Min.	−8.3	−8.6	−7.9	−8.0	−59.3	−59.7	−56.3	−58.3	5.6	7.0	4.5	1.9
Fifth percentile	−8.3	−8.5	−7.9	−8.0	−59.3	−59.7	−56.2	−58.1	5.9	7.2	4.9	2.2
Mean	−8.1	−8.3	−7.4	−7.5	−57.8	−58.2	−53.0	−55.2	7.1	8.1	6.5	4.5
Median	−8.2	−8.4	−7.8	−7.5	−58.5	−59.2	−55.0	−55.1	7.2	8.0	6.6	4.8
95th percentile	−7.6	−7.8	−6.2	−6.9	−55.0	−54.0	−45.0	−52.5	8.0	9.0	7.5	6.4
Max.	−7.5	−7.7	−5.9	−6.8	−54.1	−52.1	−42.5	−52.4	8.1	9.1	7.6	6.5
SD	0.3	0.3	0.9	0.6	1.8	2.7	5.9	3.0	0.8	0.7	1.2	2.1
Effluent-impacted streams (Teltowkanal, Nordgraben, Panke[b)])												
n	5	7	7	6	5	7	7	6	5	7	7	6
Min.	−7.6	−7.7	−7.4	−7.8	−55.4	−55.9	−54.1	−56.8	0.9	3.2	3.7	1.9
Fifth percentile	−7.5	−7.7	−7.4	−7.7	−55.4	−55.7	−54.0	−56.3	0.9	3.2	3.8	2.0
Mean	−6.9	−7.3	−7.2	−7.2	−52.5	−54.4	−53.2	−53.7	2.4	4.2	4.4	3.5
Median	−6.6	−7.4	−7.2	−7.3	−51.4	−55.0	−53.3	−54.9	1.4	4.3	4.5	3.9
95th percentile	−6.4	−7.0	−7.0	−6.6	−50.7	−53.0	−52.1	−50.9	4.9	5.7	5.1	5.0
Max.	−6.4	−7.0	−7.0	−6.6	−50.6	−52.9	−51.9	−50.9	5.1	5.9	5.1	5.5

TABLE 4 (Continued)

	$\delta^{18}O$ (‰ VSMOW)				δD (‰ VSMOW)				d-excess (‰ VSMOW)			
	Oct 18	Jan 19	May 19	Jul 19	Oct 18	Jan 19	May 19	Jul 19	Oct 18	Jan 19	May 19	Jul 19
SD	0.5	0.3	0.2	0.4	2.2	1.2	0.8	2.3	1.9	1.0	0.5	1.2
Groundwater												
n	0	7	10	8	0	7	10	8	0	7	10	8
Min.	n.a.	−8.9	−9.1	−9.2	n.a.	−63.5	−63.4	−64.7	n.a.	3.6	4.6	3.8
Fifth percentile		−8.8	−9.1	−9.1		−63.2	−63.3	−64.3		4.0	5.2	4.1
Mean		−8.1	−8.5	−8.5		−58.9	−59.5	−61.0		6.3	8.3	6.8
Median		−8.2	−8.6	−8.7		−58.9	−60.8	−62.3		6.7	8.7	7.3
95th percentile		−7.2	−7.4	−7.5		−53.9	−53.8	−55.7		8.0	10.3	8.7
Max.		−7.0	−7.1	−7.2		−52.4	−51.8	−54.0		8.2	10.7	8.8
SD		0.6	0.7	0.7		3.7	3.7	3.6		1.6	1.8	1.9

Note: Locations marked (a) at entry into the city area and (b) further downstream.

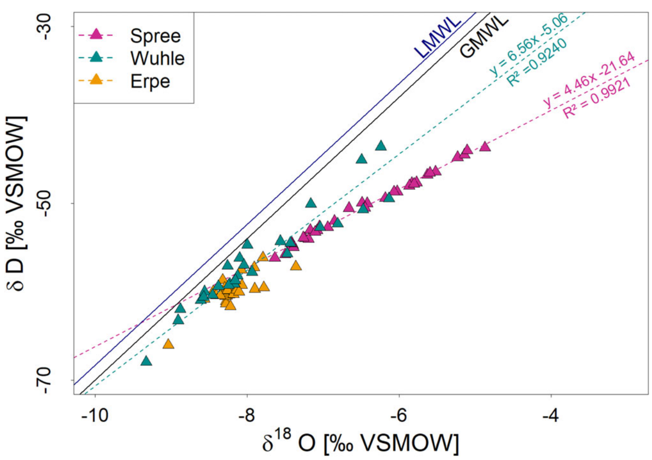

FIGURE 4 Dual isotope plot of the weekly streamwater samples compared to the global meteoric water line and local meteoric water line from Berlin-Friedrichshagen

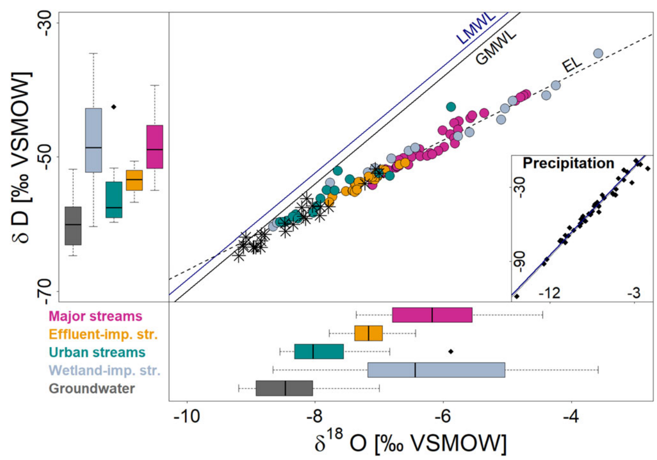

FIGURE 5 Dual isotope plot (centre) and box plots (left, bottom) showing the isotopic composition of the different surface water types and groundwater during the four seasonal sampling campaigns. global meteoric water line and amount-weighted local meteoric water line from precipitation samples in Berlin-Friedrichshagen (inset) are given for reference

18.43 ± 0.50 (R^2 = 0.9699) well below the GMWL and the LMWL. Similarly, the majority of the groundwater samples plots along this EL, though most cluster close to the LMWL.

Spatial variation in streamwater isotopes could be observed, especially in the major streams during the warmer periods in October 2018 and July 2019 (Figure 6, Figure 7). In October 2018, the enriched isotopic composition of the Spree and Dahme in the SE became slightly more depleted as the Spree flowed westwards and received water from more depleted streams like the Wuhle, Panke and Erpe. Below the Spree confluence with the even more enriched Havel, the Spree largely overprinted the signature of the Havel due to its higher discharge rates (Figure 2, Figure 6).

All major and local wetland-impacted streams were characterized by negative d-excess in October 2018 (Figure 7). While overall stream isotopic composition was more depleted in both January and May, Lake Tegel and the Fenngraben still showed more enriched values and low d-excess in January. In July, major streams became more enriched again (Figure 6). The spatial patterns resembled October 2018, however, the waters were not as enriched. The only exception was Tegeler Fließ, which showed stronger enrichment and more negative d-excess in July (Figures 6 and 7). For local urban streams, groundwater and the effluent-impacted streams, neither a spatial nor seasonal trend could be observed.

4.3 | Seasonal dynamics and spatial patterns in water chemistry

Hydrogeochemical parameters (Table 5) provided additional insights into the seasonal variability of Berlin's surface and subsurface waters.

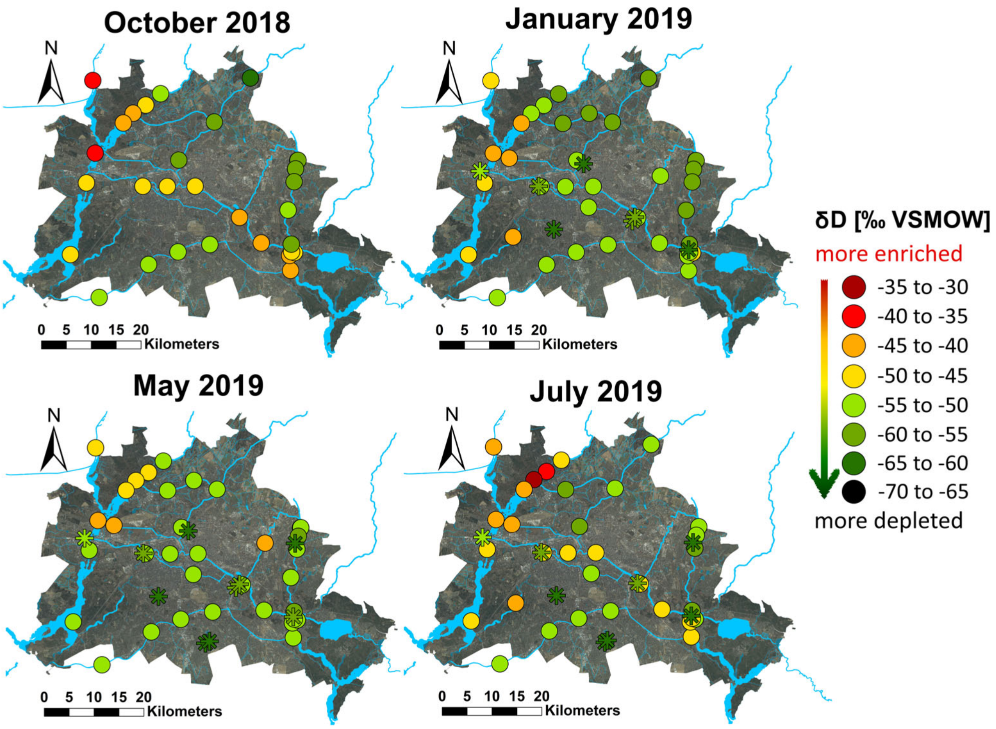

FIGURE 6 Maps showing the δD values measured in surface water (circle) and groundwater (asterisk) during the different seasonal sampling campaigns. Data source basemap: Geoportal Berlin (2018), GeoBasis-DE/BKG (2013)

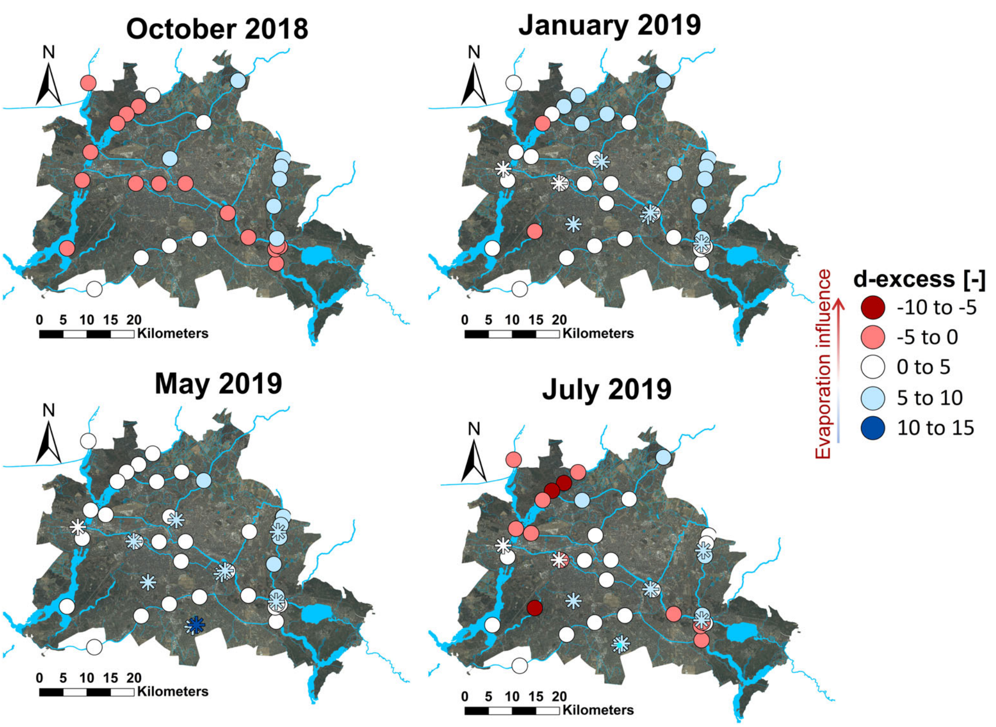

FIGURE 7 Maps showing the d-excess in surface water (circle) and groundwater (asterisk) during the different seasonal sampling campaigns. Data source basemap: Geoportal Berlin (2018), GeoBasis-DE/BKG (2013)

The pH of all surface waters was circumneutral with mean values between 7.5 and 8.2, with groundwater being slightly lower. EC was more variable in surface waters, revealing pronounced differences between seasons and sampling groups. In major streams, EC was lowest with means between 767 μS/cm in January and 880 μS/cm in July. Higher EC (1,073–1,175 μS/cm) was observed in effluent-impacted streams. In local tributaries, EC was highest in October with mean values of 1,050 μS/cm in wetland-impacted streams and 923 μS/cm in urban streams. Mean groundwater EC was high and exceeded 1,000 μS/cm during all seasons. Surface water temperatures varied

TABLE 5 Measured hydrochemical parameters in the different stream types and groundwater during the four seasonal sampling campaigns

	pH				El. conductivity (EC) (µS/cm)				Water temperature (°C)				Dissolved oxygen (DO) (mg/L)			
	Oct 18	Jan 19	May 19	Jul 19	Oct 18	Jan 19	May 19	Jul 19	Oct 18	Jan 19	May 19	Jul 19	Oct 18	Jan 19	May 19	Jul 19
Major surface waters (Dahme, (Müggel-) Spree, Havel, Lake Tegel, Landwehrkanal, Berlin-Spandauer-Schiffahrtskanal)																
n	14	16	16	16	14	16	16	16	n.a.	16	16	16	n.a	16	16	16
Min.	7.2	7.7	7.4	7.1	485	538	512	469		1.0	11.4	25.1		11.4	6.2	5.7
Fifth percentile	7.4	7.7	7.5	7.6	507	545	565	543		1.2	11.5	25.1		12.0	6.3	5.8
Mean	7.6	8.0	7.7	8.1	780	767	789	880		1.7	12.7	26.1		12.7	8.0	8.9
Median	7.6	8.0	7.7	8.1	813	818	838	940		1.7	12.8	26.1		12.8	7.8	8.8
95th percentile	7.7	8.1	8.0	8.6	960	901	906	1,114		2.5	13.9	26.9		13.2	10.0	12.0
Max.	7.7	8.1	8.3	8.7	939	912	912	1,286		2.5	14.1	27.0		13.2	12.2	12.8
SD	0.1	0.1	0.2	0.4	142	126	124	220		0.5	0.7	0.6		0.4	1.5	1.9
Local wetland-impacted streams (Tegeler Fließ, Fenngraben, Panke[a])																
n	4	5	4	5	4	5	4	5	n.a	5	4	5	n.a	5	4	5
Min.	7.6	7.8	8.1	7.8	965	827	954	693		0.2	9.9	21.4		10.4	9.7	1.2
Fifth percentile	7.6	7.8	8.1	7.8	970	851	955	713		0.3	10.1	21.9		10.4	9.9	1.6
Mean	7.7	7.9	8.2	7.9	1,050	963	969	882		1.3	11.0	24.6		11.2	11.1	5.0
Median	7.7	7.9	8.2	7.9	1,028	968	963	872		0.8	11.4	25.2		11.3	11.5	5.8
95th percentile	7.9	7.9	8.3	8.1	1,162	1,071	987	1,097		2.6	11.6	26.5		12.1	12.0	7.7
Max.	7.9	7.9	8.3	8.1	1,181	1,093	990	1,145		2.8	11.6	26.6		12.1	12.1	8.0
SD	0.2	0.1	0.1	0.1	95	95	19	168		1.0	0.9	2.1		0.8	1.2	2.7
Local urban streams (Wuhle, Marzahn-Hohenschönhausener-Grenzgraben)																
n	7	7	8	4	7	7	8	4	n.a	7	8	4	n.a	7	8	4
Min.	7.4	7.4	7.7	7.4	773	463	740	684		0.4	6.4	20.3		8.0	5.5	1.2
Fifth percentile	7.4	7.5	7.7	7.4	798	536	759	697		0.5	6.5	20.6		8.0	5.5	1.8
Mean	7.7	7.7	7.8	7.6	923	807	928	815		1.5	7.4	22.2		10.8	7.5	4.7
Median	7.6	7.7	7.8	7.6	903	857	857	819		1.7	7.4	22.4		11.0	7.4	5.6
95th percentile	7.9	7.9	8.0	7.7	1,049	965	1,228	926		2.3	8.4	23.6		13.3	9.5	6.4
Max.	7.9	7.9	8.0	7.7	1,080	966	1,311	936		2.4	8.6	23.8		13.5	9.7	6.5
SD	0.2	0.2	0.1	0.1	98	175	222	111		0.7	0.8	1.5		2.3	1.9	2.4
Effluent-impacted streams (Teltowkanal, Nordgraben, Panke [b])																
n	5	7	7	6	5	7	7	6	n.a	7	7	6	n.a	7	7	6
Min.	7.3	7.5	7.4	7.4	1,046	900	916	1,045		3.3	13.0	21.2		7.2	5.2	4.7
Fifth percentile	7.4	7.5	7.4	7.4	1,050	912	934	1,060		3.4	13.0	21.9		7.8	5.6	4.8
Mean	7.5	7.7	7.6	7.6	1,134	1,073	1,138	1,175		4.9	14.1	24.0		9.7	7.2	6.3
Median	7.5	7.7	7.6	7.6	1,087	1,170	1,233	1,187		4	13.5	24.2		10.1	7.0	6.1
95th percentile	7.7	7.8	7.9	7.9	1,265	1,184	1,245	1,277		7.7	16.1	25.5		10.8	8.8	8.0
Max.	7.7	7.8	7.9	8.0	1,269	1,185	1,245	1,280		8	16.3	25.6		11	9.0	8.2
SD	0.1	0.1	0.2	0.2	100	132	142	85		1.9	1.3	1.4		1.2	1.3	1.3
Groundwater																
n	0	7	10	8	0	7	10	8	0	7	10	8	0	7	10	8
Min.	n.a.	6.8	6.8	7.2	n.a.	879	539	536	n.a.	10.5	10.6	11.0	n.a.	0.1	0.2	0.2
Fifth percentile		6.9	6.9	7.2		893	673	663		10.5	10.6	11.5		0.1	0.2	0.2
Mean		7.2	7.1	7.4		1,471	1,311	1,111		11.8	12.1	12.9		0.4	0.5	0.7
Median		7.1	7.1	7.3		1,497	1,139	980		12.2	12.3	13.3		0.3	0.3	0.5
95th percentile		7.4	7.4	7.5		2,233	2,250	1,622		13.1	13.3	13.7		0.8	1.3	1.7
Max.		7.4	7.4	7.5		2,500	2,500	1,660		13.2	13.4	13.7		0.9	1.5	1.9
SD		0.2	0.2	0.1		542	596	373		1.2	0.9	0.9		0.3	0.4	0.7

Note: Locations marked (a) at entry into the city area and (b) further downstream.

seasonally. In both the major and local streams, means ranged from 1.3 to 1.7°C in January up to 22.2–26.1°C in July. In effluent-impacted streams, means were higher in January (4.9°C) and May (14.1°C). Groundwater temperatures were stable ~11–13°C all year. DO in surface water also varied seasonally (reflecting temperature and biological productivity) and was highest in January with means of 9.7–12.7 mg/L. Except for major surface waters, lowest DO occurred in July (4.7–6.3 mg/L). In groundwater, mean DO remained below 1 mg/L.

Regarding the major ions, the major streams had a tendency towards being Ca-SO_4-type, while local streams and groundwater were more of a Ca-HCO_3 type and effluent-impacted streams had an intermediate composition, which trended more towards a stronger Na-Cl influence (Figure 8).

In the PCA integrating all analysed data (Figure 9), the selected first five dimensions respectively accounted for 93% (October), 87% (January and May) and 90.6% (July) of the variability. For the first PC, EC (October), stable isotopes (January, May, July) and Ca-HCO_3 (July) were the main contributors. For the second PC, Na in combination with Cl, Ca-HCO_3, K, B and Cl were most important. Besides the correlation with Na and Cl, the effluent-impacted streams showed elevated K and NO_3 during all seasons (Figure 9). Additionally, a positive correlation with Boron could be observed in January and July. In the local urban streams, a correlation with elevated Phosphorus was observed, except in May. To some extent, the groundwater samples seemed to correlate with a higher Silica content.

5 | DISCUSSION

5.1 | What are Berlin's isotope dynamics in precipitation and streamwater over the course of the year?

Surprisingly few studies have applied stable isotopes in urban hydrology across scales, making this one of the first comprehensive isotope surveys in a large city. Our weighted LMWL resembled the German LMWL (Stumpp, Klaus, & Stichler, 2014) but deviated from their LMWL for Berlin by a higher intercept. This probably reflects the higher resolution of our sampling and the exceptional climate conditions. Despite this, precipitation isotopes followed the general seasonality of winter rainfall being more depleted in heavy isotopes than summer rain (see Dansgaard, 1964), though day-to-day variation could always be marked. In streamwater, these seasonal variations were damped, but to a markedly differing extent in the three reference streams sampled weekly. While the Spree was dominated by gradual, but pronounced seasonal change, the Wuhle was characterized by short-term changes in response to individual events and the Erpe was stable throughout the year. These differences are consistent with the contrasting sizes and prevailing anthropogenic influences in the catchments. In larger catchments, flow regimes are mainly controlled by the non-urban upstream catchment and travel time to the urban centre (Yang, Bowling, Cherkauer, & Pijanowski, 2011). As the Spree drains an extensive catchment upstream, regional-scale

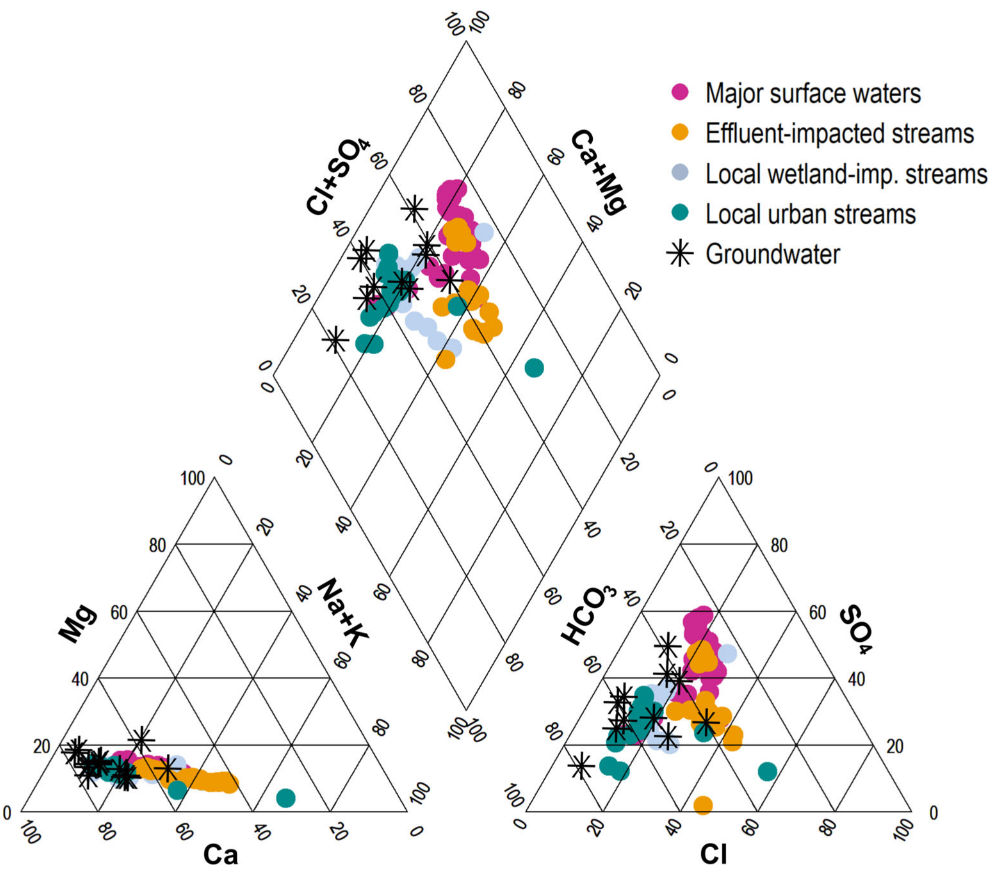

FIGURE 8 Piper plot showing the major ion composition of the water samples taken during the seasonal surveys

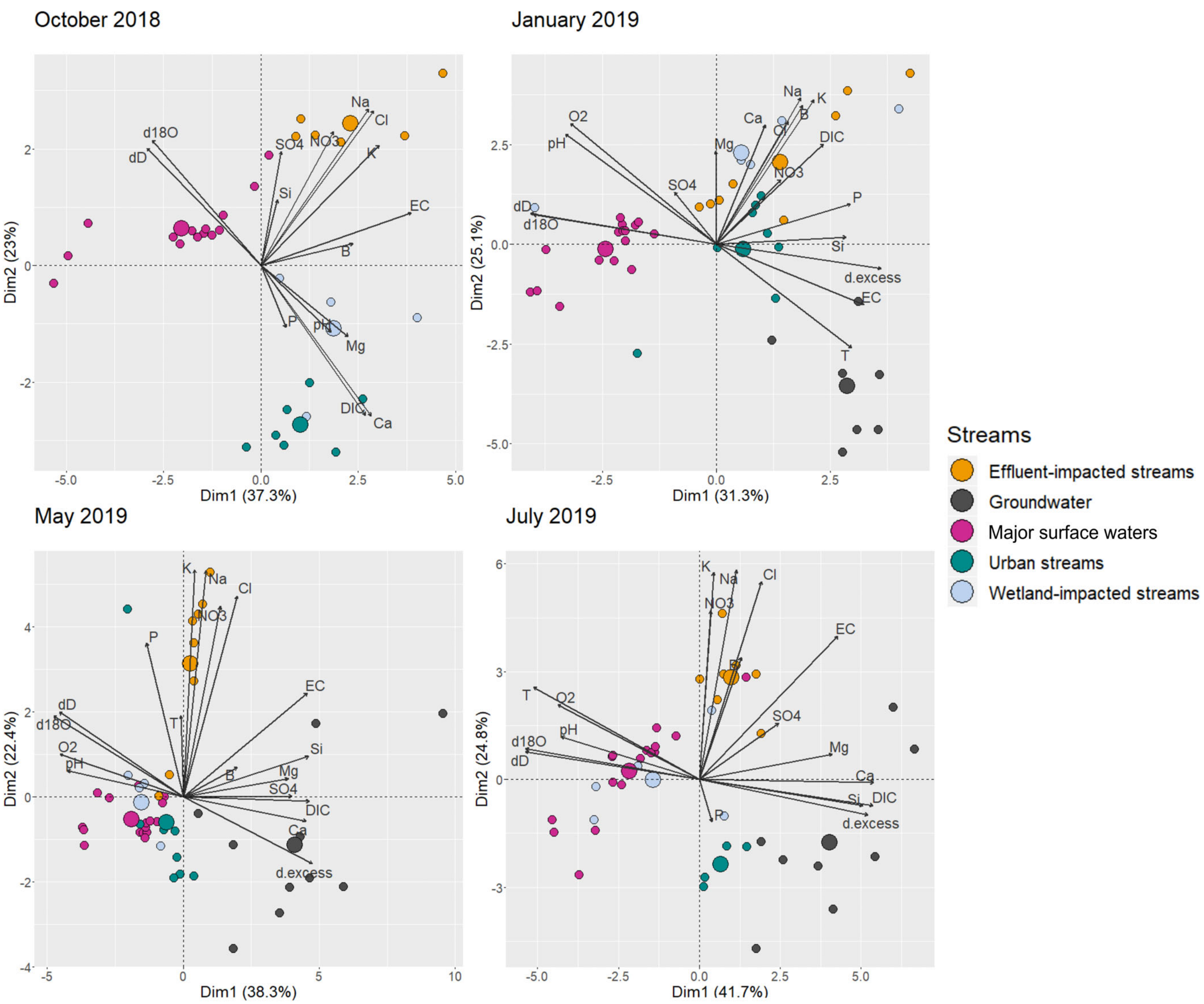

FIGURE 9 Principal component analysis comparing seasonal correlations between different measured and analysed parameters

hydroclimatic events control the flow regime and the isotopic composition of streamwater flowing into the city, though these are modulated by the large volumes of stored water in Berlin's lake systems. The effects of summer evaporative fractionation from open water areas, enhanced by low discharge and high temperatures in summer, overprint these inflows, causing samples to deviate from the MWL.

In contrast, in local urban rivers with smaller catchments like the Erpe and Wuhle, the flow regimes rather reflect the degree of impermeable cover and the structure of the urban drainage and sewer system (Roodsari & Chandler, 2017). This is consistent with recent studies suggesting that percentage impervious area, coupled with tree cover and connectivity of storm drain systems, are the major controls on hydrologic response in urban areas (Bell, McMillan, Clinton, & Jefferson, 2016; Miller et al., 2014). In such cases, urban cover can reduce mean transit times of streamwater from several years to few days (Soulsby et al., 2014) and increases the dominance of younger waters (Soulsby et al., 2015). Consequently, the Wuhle's more variable behaviour in both discharge and isotopic composition occurs as the stream responds more directly to precipitation events as urban storm drains are activated and imperviousness and urban drainage contribute substantial amounts of stream runoff. The more constant behaviour of the Erpe indicates sources with relatively unchanging isotopic composition. Most of the catchment is located outside Berlin's boundaries (Table 1) and only 21% is urban, while most land use is agriculture (65%) and forestry (14%; SenStadtUm, 2013b). Therefore, it has less direct storm drain connectivity. Given the freely-draining nature of the soils, together with shallow lateral groundwater flow above low permeability moraine (SenStadtUm, 2019), this leads to limited storm period response and a naturally groundwater-dominated flow regime. Additionally, effluents from the Münchehofe treatment plant account for 94% of summer and 55% of winter flow of the Erpe in Berlin (cf. BWB, 2019b; SenUVK, 2019), also explaining the stable discharge and isotopic composition of this stream.

5.2 | What are the spatio-temporal isotope patterns of Berlin's surface and subsurface waters during different seasons and wetness conditions?

The short-term hydrological responses of the Spree, Erpe and Wuhle provide a context for understanding the large-scale seasonal patterns and changes revealed by the synoptic surveys. Summer 2018 was the warmest recorded in NE Germany with a precipitation deficit of more than 40% compared to the long-term mean (Imbery et al., 2018). Sampling after such exceptional conditions, including a summer with heavy convective rainfall events, provided a unique opportunity to monitor the drought effects and subsequent recovery of hydrological conditions over a large urban area.

The enriched isotopic composition of Berlin's major surface waters in October 2018 and July 2019 was particularly striking and indicates significant evaporative losses from lakes and river channels. The effects of non-equilibrium fractionation are evident in the widely distributed negative d-excess (Dansgaard, 1964). While flows had increased by January, the "memory effect" of this summer evaporation was still evident in enriched isotope values in the major rivers, and was not reset until May 2019, although d-excess was positive by January. The wetland-impacted urban streams also showed evaporation effects during the October and July surveys. Here, saturated wetlands and fen soils within the catchments may contribute to strong evaporation effects in streams (Sprenger, Tetzlaff, Tunaley, Dick, & Soulsby, 2017). The observed fractionation signals can enhance understanding of land surface – atmosphere water and energy exchanges in urban areas. They provide the basis for quantitative evaporation estimates by mass balance approaches as they have, for example, been performed for regional lake networks in northern Canada (Gibson & Edwards, 2002).

Maps of isotopic signals provided insights into spatially distributed processes and the interactions of waters within Berlin. They showed the isotopic effect of more depleted groundwater from local tributaries on the Spree, despite their relatively low flow, and the moderation of the isotopic composition of the highly enriched Havel downstream of the Spree confluence in the west, especially during warm summers. This overprint of the Havel signature by the higher discharge of the Spree is consistent with earlier observations in western Berlin of Massmann et al. (2004).

5.3 | How can integration of isotope and hydrogeochemistry data help to assess how time-variance of urban hydrological processes influences the quantity and quality of stream flow?

Whilst isotopes clearly help in understanding and disentangling the sources and dynamics of stream flow generation in urban areas, the use of additional hydrochemical variables in the PCA helped to enrich our insights and test hypotheses on the provenance of water sources. Combining isotope and hydrogeochemical data helped elucidate the often unknown and time-variant fractionation effects of various water uses and/or wastewater treatment processes.

The Ca-SO_4-dominated water type of Berlin's major surface waters reflects the sulphate-rich water of the Spree. This results from extensive lignite mining in the Lausitz area (upstream of Berlin) and is intensified by wetland drainage, atmospheric deposition and agricultural fertilizers (Gelbrecht, Cabezas, Hupfer, & Zak, 2016; Zak et al., 2016). The isotopic similarity of more depleted local urban streams and groundwater can also be observed in the hydrogeochemical similarity of this group, particularly in summer, confirming groundwater as the primary water source of streams like the Wuhle. The important role of groundwater as a surface water source in urban areas, despite the impact of anthropogenic system components, has recently been highlighted by Follstad Shah et al. (2019). Rapid groundwater recharge and discharge responses, as they have been reported by Meriano et al. (2011) are, however, less likely in Berlin. Topographic and hydraulic gradients are low, though seasonal patterns of recharge and groundwater discharge clearly have an impact on the Spree system and its urban tributaries. Elevated phosphorous contents in urbanized streams like the Wuhle, as well as heavy metals, can originate from stormwater drainage (SenStadt, 2004).

Previous studies have utilized distinct isotopic signatures of local and imported waters from remote areas to identify urban supply source components (Houhou et al., 2010; Jameel et al., 2016; Tipple et al., 2017), or water from aquifers of different lithology (Demlie et al., 2008). In our study, a clear separation of groundwater and effluent impacts in Berlin's surface waters was not possible using isotopes alone. The similarity of the isotopic signatures of groundwater and treated effluents reflects the "closed" nature of Berlin water supplies that are derived from local aquifers and surface waters and thus, retain a similar isotopic composition. However, unlike the hydrochemical similarity of local urban streams to groundwater, effluent-impacted streams like the Teltowkanal and Nordgraben showed a positive correlation with Na, Cl, K and NO_3 during all seasons and a weak positive correlation with Boron. Elevated N and P loadings are characteristic of treated wastewater released into these streams (Möller & Burgschweiger, 2008). Similarly, Boron is indicative of treated wastewater, as it is used in detergents and usually inefficiently retained by sewage treatment plants (e.g. Fox et al., 2002).

5.4 | Wider implications

Despite numerous challenges in applying isotope tracers in large, heterogeneous urban areas, our study shows that isotopes can significantly contribute to disentangling the complex suite of hydrological processes sustaining urban streams and water resources. Though our study presented here provides a more qualitative overview of the situation in Berlin, it highlights the effectiveness of our generic approach, which can be applied in most other cities. Moreover, with increased data availability of other "emerging" micropollutants in urban waste waters (e.g. pharmaceuticals, personal care products, caffine, nicotine etc.), there is great potential for further constraining runoff sources (Stuart, Lapworth, Crane, & Hart, 2012). Conjunctive use of isotopes with such "new" tracers will provide a stronger basis for directing more intensive quantitative studies based around more specific research questions.

In Berlin, gauging stations continuously monitor climatic and hydrometric data. While these measurements provide useful quantitative information about specific water fluxes, our study provides more integrated, qualitative information on urban water sources and partitioning. By combining isotopes with other hydrogeochemical tracers, we can distinguish natural (precipitation, groundwater) and engineered urban water sources (effluent discharge, storm drains), which has recently been highlighted as a major research challenge in urban hydrology (e.g. Gessner et al., 2014; McGrane, 2016). As our weekly isotope sampling of urban streams like the Wuhle already indicated short-term variations in both stream discharge and isotopes, there is potential for higher-resolution sampling to assess the time-variant role of rainfall-runoff processes from impervious areas and urban drainage systems, especially after large storm events. This may facilitate the distinction between water from direct storm drains and the "urban karst," and a more quantitative estimation of associated water ages and contributions from water sources, including CSOs, through mixing models. The potential of using isotope data in more advanced, process-based ecohydrological models in urban areas has recently been highlighted by Bonneau, Fletcher, Costelloe, and Burns (2017). Whilst such intensive work was beyond the scope of the current study, the preliminary results reported here provided evidence for us to now undertake such (sub-daily) sampling on the Panke, which will be reported in future. Additionally, synoptic isotope sampling at a high spatial resolution at the river Erpe will complement the weekly sampling presented here and provide quantitative constraints on groundwater and waste water effluent controls on the spatio-temporal variations in stream water composition.

In many urban areas, there is an increasing trend to implement decentralized urban drainage systems and integrate low impact developments (LID) into new or existing urban structures. Such LIDs will be essential in adapting stormwater management strategies to changing precipitation patterns (Pyke et al., 2011). Their efficiency depends on runoff from impervious surfaces being directed towards pervious areas for infiltration, storage and release as baseflow or evapotranspiration (Miles & Band, 2015). While implementing such LIDs, isotope data can help constrain models to quantify the reduction in storm runoff generation and changes to groundwater recharge, together with the potential risk of pollution. Recently, several studies have highlighted the importance of local groundwater as a water source in urban areas (e.g. Follstad Shah et al., 2019; Meriano et al., 2011; Schirmer et al., 2013). Identifying groundwater as an important water source for local tributaries like the Wuhle or Erpe in our study highlights the importance to sustainably and conjunctively manage both urban surface and groundwater resources.

In this context, current trends of temperature increases and dry periods call for a much better understanding of groundwater recharge under different types of urban surfaces. This includes both leakage through impervious surfaces, and water partitioning under different types of urban green spaces. The diverse range of green spaces in urban areas (gardens, verges, parks, woodlands) has an important role in sustaining groundwater recharge and runoff generation processes, especially in water-limited regions like Berlin. Additionally, combining the effects of urban green spaces with evaporation from urban streams, which has been observed in major and smaller, local streams in our study (e.g. the Tegeler Fließ), is likely to have an important cooling mitigation on the UHI effect in cities like Berlin (e.g. Gunawardena, Wells, & Kershaw, 2017; Hathway & Sharples, 2012). Therefore, a more quantitative estimation of urban ET remains an essential research challenge to close the urban water balance. This will be crucial to optimize water use with other objectives and ecosystem services, especially when urban green space is being irrigated, in order to understand the trade-offs of such water subsidy (Gómez-Navarro, Pataki, Bowen, & Oerter, 2019). Current work at an ecohydrological observatory in Berlin-Steglitz aims to quantify water partitioning under different types of urban green spaces using stable isotopes and ecohydrological models (cf. Douinot, Tetzlaff, Maneta, Kuppel, & Soulsby, 2019; Smith, Tetzlaff, Kleine, & Soulsby, 2020).

While isotopes are clearly a valuable tool to identify water sources, our study shows that they also facilitate a better understanding of water losses in urban areas. Exceptionally warm and dry climate conditions in 2018 and 2019, as they are projected to increasingly occur in the future, resulted in significant evaporation losses and enriched isotope ratios in the Spree and Havel, which provide a major water resource for Berlin. These extensive evaporation losses are mainly determined at the large, regional scale in the upstream catchment but had significant impacts within the urban landscape that persisted for months after the climate conditions had changed. The persistence of these "memory effects" highlights the potential intensity of the impacts of climate warming on urban water resources. To secure a sustainable water supply for large urban areas like Berlin in the future, long-term and catchment-wide management strategies based on field data, linked with various kinds of hydrological models, are needed at nested scales. To conceptualize both the natural and engineered system components in more sophisticated ways, isotope data may be used to validate models used by utilities to monitor water mixing or evaporative losses in operating water networks (Tipple et al., 2017). Our current study already benefits from the cooperation between research institutions and local authorities, providing data and assistance in the city-wide, time-limited sampling process. However, understanding and managing large-scale changes in urban water resources will require the collaboration not only with water managers in the city itself, but also with authorities responsible for the upstream, usually more rural, catchments. Such collaboration will be essential for nesting large-scale studies of urban areas and in the larger context of their associated catchments.

6 | CONCLUSIONS

Stable isotopes have outstanding potential to trace water fluxes in complex urban areas across different temporal and spatial scales. Large urban rivers develop a damped response to the isotopic seasonality of rainfall and require regional-scale seasonal climatic variability to alter their isotopic composition. Effluent discharge to smaller urban streams results in a relatively stable isotopic composition. In contrast, local streams in highly urbanized areas which are connected to stormwater drainage systems show marked short-term responses to precipitation events in both discharge rates and isotope ratios. Seasonal maps of isotopes and d-excess across Berlin revealed large-scale isotope patterns and interactions of major and local streams under different wetness conditions. Most notable were the extensive evaporation losses in Berlin's major surface waters during the summer months, which were, to some extent, diluted by the confluence of local, more depleted groundwater- and effluent-impacted streams. By combining stable isotopes with hydrogeochemical data, we were able to distinguish between natural and engineered water sources, despite similar isotopic signatures of effluents and local groundwater, thereby overcoming the limitations of previous studies in urban areas relying solely on distinct isotope signatures for source identification. Besides demonstrating how isotope tracers can be used to capture a wide range of urban hydrological processes across various temporal and spatial scales, the exceptional climatic conditions during our study provide a first insight into how urban waters might react to future climate changes. Ongoing research is needed, especially to assess the time-variant rainfall-runoff behaviour of urban streams through high-resolution sampling, incorporating field data into different kinds of ecohydrological models, and to investigate the infiltration behaviour under urban green spaces to better understand urban groundwater recharge and obtain a more quantitative estimation of urban ET. While individual observations are specific to Berlin's water system, the approach used here can be usefully transferred to other metropolitan areas.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

ORCID

Lena-Marie Kuhlemann https://orcid.org/0000-0003-0541-7940
Doerthe Tetzlaff https://orcid.org/0000-0002-7183-8674
Chris Soulsby https://orcid.org/0000-0001-6910-2118

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